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CCL John H. MacMillan Chemistry Preprints

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John H. MacMillan's Chemistry Preprint Articles Research and review articles on: Liquid crystals, organometallic compounds, silanes, silicones, platinum catalysts, organophosphines, homogeneous, heterogeneous catalysts, insulating glass sealants, Grignard reagents... Complete list of papers and patents of Dr. MacMillan can be found at: <http://docs.google.com/Doc?docid=0AR2ideyPd9SLZGd3amM5ZmRfMTg3em05Z3Y5Zms&hl=en>

- [The_Acetylenic-Oxy-Cope_Rearrangement_of_1,5-Hexadiyne-3-ol_and_Methyl_Substituted_Derivatives.pdf](#) [3577kB] : The Acetylenic-Oxy-Cope Rearrangement of 1,5-Hexadiyne-3-ol and Methyl Substituted Derivatives
Vapor phase thermolysis of 1,5-hexadiyne-3-ol at 350°C afforded phenol and 4-methylene-2-cyclobuten-1-carboxaldehyde as products. The 4-methyl derivative gave only ortho cresol and 4-ethylidene-2-cyclobutene-1-carboxaldehyde. The 3-methyl and 4,4-dimethyl derivatives yielded no aromatic products. 3-Acetyl-4-methylene cyclobutene was the sole product from thermolysis of the 3-methyl derivative, while 4-isopropylidene-2-cyclobutene-1-carboxaldehyde was the sole product from thermolysis of the 4,4-dimethyl derivative. The phenol and ortho-cresol aromatic products are postulated to result from cyclization of intermediate 1-hydroxy-1,2,4,5-tetraenes (bis allenes), produced by acetylenic oxy-Cope rearrangements. Subsequent supra facial 1,5-hydrogen shifts restore the aromaticity. The 3-methyl and 4,4-dimethyl derivatives cannot aromatize by this pathway. Exclusive formation of ortho cresol eliminates prismane or benzvalene intermediates, as such structures should also produce meta and para cresols. The mechanism of cyclobutene derivative formation for all compounds is proposed to involve cyclization of the identical bis allenes, via diradical pathways. The 3-hydroxy functionality greatly facilitated the rate of the aromatizations, consistent with rate accelerations seen in other oxy-Cope and acetylenic oxy-Cope systems.
- [Addition_of_propargyl_allyl_and_benzyl_Grignard_reagents_to_alpha_beta_unsaturated_alcohols.pdf](#) [4889kB] : Addition of propargyl, allyl and benzyl Grignard reagents to α, β -unsaturated alcohols
 α, β -Unsaturated alkenyl or propargyl alcohols add propargyl, allyl and benzyl Grignard Reagent at the β -position of the alcohol, yielding methylene or methyl substituted alcohols in moderate yield. Alkenes and

alkynes with no alcohol functionality or alcohols with no α , β -unsaturated functionality failed to react. Saturated Grignards gave very low yields. The mechanism is postulated to involve a cyclic transition state with an initial complex of the hydroxyl on the alcohol to the magnesium of the Grignard. The reaction has synthetic utility for the production of 2-methylene substituted alcohols.

- [Addition_of_propargyl_Grignard_to_aldehyde_1-Phenyl-3-butyne-1-ol.pdf](#) [580kB] : Addition of propargyl Grignard to aldehyde; 1-Phenyl-3-butyne-1-ol
In order to avoid an internal rearrangement of the propargyl Grignard reagent, a modification of the procedure reported by Sondheimer was utilized. The procedure involved low temperature preparation of the Grignard reagent, catalyzed by mercuric chloride. For example, without this modification, a room temperature standard Grignard synthesis of 1-hexen-5-yne-3-ol gave an approximate 50/50 mixture of desired product and the rearranged internal alkyne product 1-hexen-4-yn-3ol. This reaction gives reproducible yields in the 60-80% range. No trace of product alcohols resulting from rearrangement of propargyl Grignard to internal acetylenic or allenic species could be detected under these conditions.
- [Acetylenic_Alcohols.pdf](#) [940kB] : Preparation of acetylenic alcohols by addition of propargyl Grignard reagents activated at low temperatures with mercury ion to α,β -unsaturated aldehydes and ketones. *Addition of propargyl Grignard reagents to α,β -unsaturated aldehydes and ketones, with Grignards synthesized at low (-30 to -10 o C) temperatures and activated at these temperatures by trace amounts of mercuric chloride, gave acetylenic alcohols in good yields. No trace of products resulting from rearrangement of propargyl Grignards to internal acetylenic or allenic species could be detected. In contrast, room temperature reactions gave alcohol product mixtures resulting from the rearrangement of propargyl Grignards to internal alkynyl or allenyl Grignards. This synthetic modification is of great utility in preparation of alcohol precursors for annulene synthesis or acetylenic oxy Cope rearrangements.*
- [Facile_N-methylation_of_amide_functional_heterocycles_with_dimethyl_sulfate.pdf](#) [893kB] : Facile N-Methylation Reaction of Amide Functional Heterocycles with Dimethyl Sulfate.
4 and 5-substituted 1,3(3H) oxazine-2,6-diones (oxauracils) are easily alkylated under mild conditions with dimethyl or diethyl sulfate in boiling acetone and slurry of sodium bicarbonate. Workups are straight forward and yields typically in the 60-70% range. The reaction should prove of utility also for alkylating uracils and other amide functional heterocycles.
- [Chiral-Liquid-Crystalline-Nitrones.pdf](#) [6124kB] : Preparation, mesogenic behavior and photochemistry of homologous chiral liquid crystalline nitrones.
*A series of chiral N-(*p*-2-methoxybutoxyphenyl)- α -(*p*-*n*-alkoxyphenyl) nitrones, was prepared and examined for mesogenic properties. The methyl derivative showed only a transient cholesteric texture on rapid supercooling, while the ethyl homolog was a monotropic cholesteric. The propyl and butyl homologs were non mesogenic while the pentyl derivative showed a monotropic chiral Sc mesophase. The higher members of the series were enantiotropic, exhibiting only chiral Sc mesophases. The materials exhibited both thermal and photochemical instability, however, suitable eutectization resulted in lower temperature chiral Sc and cholesteric phases with adequate stability under long wavelength (> 400 nm) illumination.*
- [ArylmaleicAnhydrides.pdf](#) [2501kB] : Detailed synthetic procedures for arylmaleic anhydrides; *p*-bromophenyl maleic anhydride and other aryl substituted maleic anhydrides.

Detailed synthetic procedures and spectral data for the synthesis of aryl substituted maleic anhydrides are listed.

- [Synthesis_of_unreported_4- and_5-Aryl_Substituted_1,3\(3H\)_Oxazine-2,6-Diones.pdf](#) [2264kB] : Detailed Synthetic Procedure for 4-(4-bromophenyl)-1,3(3H) Oxazine-2,6-Dione and related 4 and 5-aryl substituted -1,3(3H) Oxazine-2,6-Diones
Spectroscopic and analytical data are included.
- [Reaction-of-acrylonitrile-with-trimethylsilyl-azide.pdf](#) [922kB] : The Reaction of Acrylonitrile with Trimethylsilyl Azide
Acrylonitrile (1) on reaction with trimethylsilyl azide (2) gave complex mixtures, with 3-imino-2-trimethylsilyl propionitrile (4) being the major isolatable product in low yield. The reaction was slow even in high boiling solvents due to the electron withdrawing cyano group decreasing the nucleophilicity of the conjugated double bond. Considerable intractable polymer was always produced. The mechanism is believed to involve anti-Markonikov 1,2 addition of trimethylsilyl azide (2) to the double bond of 1, giving intermediate 3-azido-2-trimethylsilyl propionitrile (3). Loss of nitrogen gives imine (4). The mechanism is supported by the detection of an intermediate believed to be 3 on g.c. analysis, which rapidly disappeared giving 4. The reaction is of limited synthetic utility due to the slow rate and tendency of acrylonitrile to polymerize even with inert solvent added as diluent.
- [reaction_naphthoquinones_with_trimethylsilyl_azide.pdf](#) [271kB] : Further Studies of the Interaction of Carbonyl Compounds with Organometallic Azides, the Reaction of Naphthoquinones with Trimethylsilyl Azide.
1,4-Naphthoquinone and 1,2 Naphthoquinone on reaction with trimethylsilyl azide gave complex mixtures, with 2-amino-1,4-naphthoquinone and 4-amino-1,2-naphthoquinone being the major isolatable products. The mechanism is believed to involve conjugate 1,4 addition of trimethylsilyl azide to an α,β -unsaturated carbonyl carbon, giving intermediate trimethylsiloxy azide adducts. Loss of nitrogen gives imine intermediates, which on hydrolysis and tautomerization give amino naphthoquinones. The mechanism is supported by the isolation of an adduct of the proposed intermediate with 1,4-naphthoquinone. Anthraquinone fails to react, also consistent with this mechanism, as 1,4 addition of trimethylsilyl azide would disrupt the aromaticity of one ring.
- [aryl-oxauracils.pdf](#) [46kB] : Synthesis of Additional 4 and 5-Aryl Substituted 1,3(3H) Oxazine-2,6-Diones. Additional 4-and 5-Aryl Substituted 1,3(3H) oxazine-2,6-diones (oxauracils) were synthesized for anti malarial screening by the reaction of the corresponding aryl maleic anhydride with trimethylsilyl azide, by the procedure described in J. Heterocyclic Chemistry, Vol. 12, p 1215, (1975). The N-Alkylated derivatives were prepared by refluxing the corresponding aryl substituted oxauracil with a di alkyl sulfate/sodium bicarbonate slurry in acetone, as described in the above paper.
- [EuFOD-Shift-Data.pdf](#) [5850kB] : Supplemental Unpublished Original Notebook Chemical Shift Data Supporting J.H. MacMillan and S.S. Washburne,
This material is additional supplemental original notebook chemical shift data supporting J.H. MacMillan and S.S. Washburne, "Lanthanide Chemical Shift Reagents as Tools for Determining Isomer Distributions in 2,4-Hexadieneoates and Related Compounds", Organic Magnetic Resonance, Vol.6, p250,(1974). This

research was performed at Temple University in 1973, sponsored under Grant No. CA-1 3120-02 from the National Cancer Institute. The original notebook entries were scanned for this document. They are handwritten but nearly all legible.

- [phenyl.pdf](#) [1215kB] : Investigation of Possible Phenyl Participation in the Oxy-Cope and Acetylenic Oxy-Cope Rearrangements.
Vapor Phase thermolysis of 1-phenyl-3-butyn-1-ol and 1-phenyl-2-methyl-3-butyn-2-ol in the gas phase or liquid phase failed to yield the expected oxy-Cope products, even at elevated temperatures and with protracted reaction times. 1-Phenyl-3-butyn-1-ol cleaved to benzaldehyde and allene, while 1-phenyl-2-methyl-3-butyn-2-ol was completely unreactive. The data indicate that the disruption of the aromatic ring necessary for the Oxy-Cope reaction to occur results in too high an activation energy. Claisen Rearrangements, by contrast, proceed readily under these conditions. The activating effect of the ether oxygen atom in Claisen rearrangements may lower their activation energy compared to oxy-Cope systems.
- [virtual-laboratory.pdf](#) [115kB] : Virtual Chemistry Laboratory for Non-Science Majors, Good, Bad or Both?
The author's experiences with a totally virtual chemistry laboratory versus the traditional hands on laboratory are summarized and analyzed, together with the advantages and disadvantages of both approaches. A compromise program is favored, where computerized instruction is integrated with the classical program, both to minimize lab costs for the school or University, and to provide real world lab experience for the students.
- [constructivist.pdf](#) [155kB] : Constructivist (hands on) theories for high school chemistry curricula are reviewed and critiqued. The authors own experiences with this learning technique are described. Advantages and disadvantages of constructivist learning versus traditional chemistry education are discussed.
- [Tufts-Thesis.pdf](#) [7265kB] : John H. MacMillan, Undergraduate Thesis, Tufts University, 1966
Subjects: Vanadium Hydride, Palladium Hydride, Vanadium Hydride X-ray line broadening, Magnetic Susceptibility of Palladium Hydride, Non Stoichiometric Hydrides.
- [The Magnetic Susceptibility of Palladium Hydride J. Phys. Chem. Vol. 70 p3024 1966.pdf](#) [114kB] : MacMillan Publication 1
- [Vapor Phase Thermolysis of 1-Hexen-5-yn-3-ol An Acetylenic Oxy-Cope Reaction J. Amer. Chem. Soc. Vol. 90 p. 6141 1968.pdf](#) [700kB] : MacMillan Publication 2
- [A Novel Steric Effect in the Thermolysis of Prop-2-ynyl Vinyl Carbinols Chemical Communications p. 301 1970.pdf](#) [200kB] : MacMillan Publication 3
- [The Vapor Phase Acetylenic Oxy-Cope Reaction of 5-Hexen-1-yn-3-ol The Chemistry of an Allenol Intermediate J. Amer. Chem. Soc. Vol. 92 p. 2404 1970.pdf](#) [1079kB] : MacMillan Publication 4
- [Participation of Acetylenic Bonds in Pericyclic Reactions Thermal Cleavage of Beta-Hydroxyacetylenes J. Amer. Chem. Soc. Vol. 93 p. 6967 1971.pdf](#) [1352kB] : MacMillan Publication 5

- [Reaction_Rates_by_Flow_System_Thermolysis_The_Competitive_Components_of_the_Oxy-Cope_Reaction_Chemical_Communications_p_936_1971.pdf](#) [232kB] : MacMillan Publication 6
- [Interaction_of_Carbonyl_Compounds_with_Organometallic_Azides_Part_V._Sorboyl_Chloride_and_its_Conversion_to_an_Alpha-Pyridone_J._Org._Chem._Vol._38_p_2982_1973.pdf](#) [443kB] : MacMillan Publication 7
- [Lanthanide_Chemical_Shift_Reagents_as_Tools_for_Determining_Isomer_Distributions_in_2,4-Hexadiene-oates_and_Related_Compounds_Organic_Magnetic_Resonance_Vol._6_p250_1974.pdf](#) [294kB] : MacMillan Publication 8
- [Recent_Examples_of_Selectivity_in_Catalysis_Strem_Chemiker_Vol._11_No._2_July_1974.pdf](#) [1307kB] : MacMillan Publication 9
- [Synthesis_of_Substituted_2H-1,3-Oxazine-2,6-Diones_by_Reaction_of_Trimethylsilyl_Azide_with_Maleic_Anhydrides_J.Org.Chem._Vol._40_p_743_1975.pdf](#) [556kB] : MacMillan Publication 10
- [Further_Investigation_of_the_Interaction_of_Trimethylsilyl_Azide_with_Substituted_Maleic_Anhydrides_Synthesis_of_4-and_5-Aryl_Substituted_1,3,3H_Oxazine-2,6-Diones_J.Heterocyclic_Chemistry_Vol._12_p_1215_1975.pdf](#) [677kB] : Publication Number 11
- [Improved_Procedure_for_the_Preparation_of_Oxauroacil_2H-1,3,3H-Oxazine-2,6-Dione_Organic_Preparations_and_Procedures_Int._Vol_9._p_87_1977.pdf](#) [198kB] : Publication Number 12
- [Low_Transition_Temperature_Liquid_Crystalline_Amines_Incorporating_the_Trans-1,4-Cyclohexane_Ring_System_Molecular_Crystals_and_Liquid_Crystals_Vol._55_p_61_1979.pdf](#) [804kB] : Publication Number 13
- [Induced_Phases_in_Terminal_Mixtures_of_Polar_Liquid_Crystalline_Amines_and_Nitriles_Mol._Crystals_and_Liquid_Crystals_Letters_Vol._56_p7_1979.pdf](#) [322kB] : Publication Number 14
- [Low_Transition_Temperature_Liquid_Crystalline_Amines_Incorporating_the_Biphenyl_Ring_System_Mol._Crystals_and_Liquid_Crystals_Letters_Vol._56_p51_1979.pdf](#) [394kB] : Publication Number 15
- [Amine_Substituted_Liquid_Crystal_Compositions_U.S._Patent_4_293_193_Oct._6_1981.pdf](#) [335kB] : MacMillan U.S. Patent Number 1
- [One_Package_Heat_Curable_Sealant_Compositions_U.S._Patent_4_430_489_Feb._7_1984.pdf](#) [762kB] : MacMillan U.S. Patent Number 2
- [Thioether_Modified_Polymer_Compositions_U.S._Patent_4_590_240_May_20_1986.pdf](#) [530kB] : MacMillan U.S. Patent Number 3
- [Method_for_the_preparation_of_aminopropyl_or_aminoalkyl_functional_polyalkyl_or_aryl_siloxanes_United_States_Patent_6_177_583_January_23_2001.pdf](#) [347kB] : MacMillan U.S. Patent Number 4
- [Siloxane_modified_carboxylic_acid_substituted_amines_and_salts_thereof_U.S._Patent_6_489_499_December_3_2002.pdf](#) [479kB] : MacMillan U.S. Patent Number 5

- [Supported aldehydic silanes and method of manufacture_U.S. Patent 6 589 799 July 8 2003.pdf](#) [446kB] : MacMillan U.S. Patent Number 6
- [Supported aldehydic silanes and method of manufacture_U.S. Patent 7 045 365 May 16 2006.pdf](#) [545kB] : MacMillan U.S. Patent Number 7
- [One Package Heat Curable Sealant Compositions_U.S. Patent 4 430 489 Feb. 7 1984.pdf](#) [762kB] : MacMillan U.S. Patent Number 12
- [Japanese-Strem-Chemiker-1974.pdf](#) [5654kB] : Japanese Edition of "Recent Examples of Selectivity in Catalysis", by John H. MacMillan, Strem Chemicals, July, 1974.
- [Vanadiun-Line-Broadening.pdf](#) [3003kB] : **T.R.P. Gibb Jr. and John H. MacMillan**, Vanadium hydride x-ray line broadening
The broadening of the x-ray diffraction lines of non stoichiometric vanadium hydrides of composition VH0.15 to VH0.80 were measured and compared to pure vanadium powder. The 110,200,211,220,310 and 321 diffraction planes line broadening were measured at all stoichiometries. In every case the 211 plane showed the greatest percentage broadening, followed by the 200 plane. The broadening order was 211>200>110=310>321.
- [bioconext.pdf](#) [42kB] : A method for derivatizing surfaces with aldehyde groups by employing a new alkoxy aldehydic silane. **Coyne, Ann. N., Benner, Lauren., MacMillan, John H., Telepchak, Michael T.** A new line of trialkoxy aldehydic silanes, manufactured by United Chemical Technologies, Inc. under the trademark BIO-CONEXT, allows the one-step addition of an activated surface directly to a matrix, thus circumventing the steps and reagents required by other methods. In addition, the covalent linkage formed by this method has only one Schiff base, yielding a much more stable product. Furthermore, this method can be used with any matrix that has either naturally occurring or synthetically incorporated hydroxyl groups that can be synthetically modified with trialkoxy aldehydic silanes. Included are some of the most popular and useful matrix materials, such as glass, agarose, silica, glass-coated ELISA plates, metals such as nickel and paramagnetic iron, and some commercially available resins1. In addition, incorporation of trialkoxy aldehydic silanes with different chain lengths can be used to prevent crowding of large bio-molecules and to allow access to active sites. In this report, we describe and evaluate the BIO-CONEXT method for covalent attachment of bio-molecules.
- [Nitrones-2.pdf](#) [3076kB] : Synthesis and Photochemistry of Chiral Liquid Crystalline Nitrones
- [Grignard-addition-to-propargylic-allylic-alcohols.pdf](#) [1467kB] : Addition of Grignard Reagents to Allylic and Propargylic Alcohols
- [adhesion.pdf](#) [408kB] : Using Silanes as Adhesion Promoters
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- [tmsa-benzoquinone-4.pdf](#) [819kB] : Further Studies of the Interaction of Carbonyl Compounds with Organometallic Azides, the Novel Reaction of Benzoquinone with Trimethylsilylazide
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- [diphenylacetylene2.pdf](#) [401kB] : An Improved Method for the Preparation of Bis-DiphenylPhosphino Acetylene and unsymmetrical Aryl Substituted Diphenylphosphino Acetylenes
- [polyformals-2.pdf](#) [3415kB] : Hexamethylene Glycol Polyformal Copolymers for Insulating Glass and Building Sealants
- [ArylMaleic-Anhydrides.pdf](#) [2185kB] : A Facile General Synthesis of Arylmaleic Anhydrides:
By a sequence involving Knoevenagel condensation, Michael addition of cyanide, hydrolysis, and selenium dioxide oxidation, a series of seven aryl maleic anhydrides were prepared in excellent overall yields. The regiospecificity of reaction of these anhydrides with various nucleophilic species, e.g. Me3SiN3, NH3, and PhNH2 was investigated. Except for a few cases, the nucleophile attacks the more hindered carbonyl, in a reaction controlled by electronic rather than steric factors. These anhydrides are of particular utility in the synthesis of 4-and 5-Aryl Substituted 1,3(3H) Oxazine-2,6-Diones (Oxauracils).
- [Oxauracils-Hydrolysis.pdf](#) [4903kB] : Hydrolysis reactions of the 4-and 5-Alkyl or Aryl Substituted 1,3(3H) Oxazine-2,6-Diones (Oxauracil) Ring System
Acid or base hydrolysis of 4-Aryl or alkyl Substituted 1,3(3H) Oxazine-2,6-Diones (Oxauracils)1,2 yield alkyl or aryl methyl ketones, 6, and ammonia. An intermediate beta keto acid, 5, could be isolated under mild conditions. N-alkylated oxauracils give the same methyl ketones and alkylamines. The N-alkylated oxauracils hydrolyze faster than the non alkylated oxauracils in competition experiments, probably due to electronic factors. 5-aryl oxauracils hydrolyze slower than the 4-isomers in direct competition experiments, probably due to steric factors at the C-6 carbonyl carbon. A mechanistic scheme is presented involving nucleophilic attack at the C-6 carbonyl, decarboxylation of the resulting amino acid 2 yielding enamine 3, which tautomerizes to imine 4. Hydrolysis of 4 and further decarboxylation of beta keto acid 5 give methyl ketones 6 in nearly quantitative yield. The in vitro toxicity of these products is low, thus is of little concern in genetic studies involving substitution of oxauracils for uracils in RNA or other nucleotides.
- [surface.pdf](#) [38kB] : Silane Surface Modifying Reagents
Industrial silane suppliers offer a wide range of polar and non-polar silanes which may be used to modify the surface of substrates such as glass, silica, alumina, silicon and transition metals. The surface may be treated to decrease wettability or increase adhesion of the polymer to glass, silicon or metals. Such treatment may also allow differential polar or hydrophobic interactions. The hydrophobic class represents alkyl functional alkoxy or chlorosilanes from C2-C22 chain length. They find use in decreasing the wettability of treated surfaces, as releasing agents and for increasing the hydrophobic interactions of treated sorbents with diluents in a mobile phase.

- [MacMillan_PhD_Thesis.pdf](#) [13016kB] : Triple Bond Participation in the Oxy-Cope Rearrangement (Ph.D. Thesis)

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